

Heats of Combustion and Isomerization of Six Nonanes

By Walter H. Johnson, Edward J. Prosen, and Frederick D. Rossini

The heats of isomerization of six of the nonanes were determined by measurement of the ratios of the heats of combustion in the liquid state of purified samples of these compounds by the procedure previously described for other hydrocarbons. The data yield the following values for the heat of isomerization in the liquid state at 25° C, ΔH° , of *n*-nonane into the other nonanes, in kilocalories per mole: *n*-Nonane, 0.00; 3,3-diethylpentane, -0.01 ± 0.33 ; 2,2,3,3-tetramethylpentane, -0.70 ± 0.31 ; 2,2,3,4-tetramethylpentane, -0.56 ± 0.22 ; 2,2,4,4-tetramethylpentane, -1.11 ± 0.25 ; 2,3,3,4-tetramethylpentane, -0.62 ± 0.35 . These data were combined with the value previously reported for the heat of combustion of *n*-nonane to obtain values for the heats of combustion of the other five nonanes in the liquid state at 25° C.

I. Introduction

In continuation of the program of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types [1, 2, 3, 4, 5, 6, 7]¹ calorimetric measurements have been made that yield values for the differences in the heats of combustion, or the heats of isomerization, of six of the isomeric nonanes in the liquid state at 25° C. These heats of isomerization were combined with the value [8] previously reported for the heat of combustion of *n*-nonane to obtain values for the heats of combustion of the other five nonanes in the liquid state at 25° C.

II. Unit of Energy, Molecular Weights, Uncertainties

The unit of energy upon which the values reported in this paper are based is the international joule, derived from mean solar seconds and the units of international ohms and international volts, in terms of which certification of standards of resistance and electromotive force is made by the Bureau. For conversion to the conventional thermochemical calorie, the following relation is used [9]:

¹ Figures in brackets indicate the literature references at the end of this paper.

1 calorie = 4.1833 international joules.

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of international atomic weights [10].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [11].

Definitions of the symbols used are given in previous papers [1, 3, 4, 6, 7].

III. Method and Apparatus

The same method and apparatus were used as in the investigations recently reported from this laboratory [1, 2, 3, 4, 5, 6, 7, 12]. One calorimeter system was used throughout this investigation. Resistance bridge No. 404 and platinum resistance thermometer No. 373,730 were used for all the experiments reported here.

No products of incomplete combustion were found in any of the experiments.

IV. Materials

The compounds used in the present investigation were samples from the API-NBS series of highly purified hydrocarbons, which are being prepared through a cooperative undertaking of

the American Petroleum Institute and the National Bureau of Standards [15, 16, 17].

These samples of API-NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44 on the "Collection, Analysis, Calculation, and Compilation of Data on the Properties of Hydrocarbons." The samples were purified at the National Bureau of Standards by the API Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons", from material supplied by the following laboratories:

3,3-Diethylpentane and 2,2,3,3-tetramethylpentane, by the American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord.

2,2,3,4-Tetramethylpentane, 2,2,4,4-tetramethylpentane, and 2,3,3,4-tetramethylpentane, by the National Advisory Committee for Aeronautics, through its Aircraft Engine Research Laboratory, Cleveland, Ohio, and its supported work in the Automotive Section at the National Bureau of Standards.

n-Nonane, by the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

A complete description of the purification, purity, and freezing points of the six nonanes of the present investigation is given by Streiff, Murphy, Cahill, Flanagan, Sedlak, Willingham, and Rosini [17], who reported the amounts of impurity

in these samples, as determined from measurements of freezing points, to be as follows: *n*-Nonane, 0.0006 ± 0.0004 ; 3,3-diethylpentane, 0.00013 ± 0.00011 ; 2,2,3,3-tetramethylpentane, 0.0006 ± 0.0002 ; 2,2,3,4-tetramethylpentane, 0.00024 ± 0.00014 ; 2,2,4,4-tetramethylpentane, 0.0011 ± 0.0008 ; 2,3,3,4-tetramethylpentane, 0.00044 ± 0.00037 , mole fraction.

As the manner of purification of these compounds [17] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the worst case the measured heat of combustion would be affected by less than 0.001 percent because of impurities in the compound.

V. Results

The experimental results of the present investigation are summarized in table 1, which gives for each of the six compounds the following data: The number of experiments performed; the minimum and maximum values of the mass of carbon dioxide formed in the combustion and of the calorimetric quantities k , K , U , ΔR_c , Δr_i , Δr_n [1]; the mean value of B , and its standard deviation, in ohms per gram of carbon dioxide formed, as defined by equation 4 of reference [1]. The symbols have the same significance as in the previous report [1], and the references there cited.

In table 2 are given, for the six nonanes, values of the following: The constant B in ohms per gram of carbon dioxide, as given in table 1; B° , which is B corrected to the ideal bomb reaction by the

TABLE 1.—Results of the calorimetric combustion experiments

Compound (liquid)	Number of experiments	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B	
									Mean	Standard deviation of mean
		<i>g</i>	<i>min</i> ⁻¹	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm/gCO₂</i>	<i>Ohm/gCO₂</i>
<i>n</i> -Nonane	5	[2.53916 to 2.61484	0.001979 to .001990	0.001023 to .001326	0.000227 to .000242	0.287491 to .296007	0.000415 to .000430	0.000043 to .000056	0.1130485	± 0.0000082
3,3-Diethylpentane	6	[2.53532 to 2.65980	0.001974 to .001984	0.000866 to .001271	0.000160 to .000309	0.287080 to .301067	0.000415 to .000426	0.000050 to .000054	0.1130482	± 0.0000098
2,2,3,3-Tetramethylpentane ..	6	[2.45440 to 2.56627	0.001971 to .001997	0.001154 to .001518	0.000094 to .000328	0.277761 to .290464	0.000411 to .000427	0.000050 to .000054	0.1129942	± 0.0000090
2,2,3,4-Tetramethylpentane ..	5	[2.52718 to 2.63979	0.001974 to .001984	0.000891 to .001317	0.000187 to .000291	0.286006 to .298752	0.000416 to .000430	0.000050 to .000056	0.1130049	± 0.0000026
2,2,4,4-Tetramethylpentane ..	7	[2.51035 to 2.67953	0.001976 to .001995	0.000777 to .001477	0.000162 to .000294	0.283988 to .303077	0.000415 to .000431	0.000036 to .000044	0.1129624	± 0.0000051
2,3,3,4-Tetramethylpentane ..	5	[2.53247 to 2.86449	0.001977 to .001991	0.000558 to .001427	0.000269 to .000374	0.286688 to .324037	0.000234 to .000424	0.000040 to .000046	0.1130014	± 0.0000105

TABLE 2.—Heats of isomerization and combustion in the liquid state

Compound	B, at 28.00° C	B°, at 28.00° C	Ratio of the heats of combustion in the ideal bomb proc- ess, B_i/B_n , at 28.00° C	Difference in the heats of combus- tion in the ideal bomb process $(-\Delta U^\circ)_n -$ $(-\Delta U^\circ)_i$, at 28.00° C
	<i>Ohm/gCO₂</i>	<i>Ohm/gCO₂</i>		<i>Int. kj/mole</i>
<i>n</i> -Nonane.....	0.1130485 ±0.0000164	0.1130214 ±0.0000164	1.000000	0.00
3,3-Diethylpentane.....	.1130482 ±0.0000196	.1130211 ±0.0000198	0.999997 ±0.000227	0.02 ±1.39
2,2,3,3-Tetramethylpentane.....	.1129942 ±0.0000180	.1129674 ±0.0000180	.999522 ±0.000215	2.92 ±1.31
2,2,3,4-Tetramethylpentane.....	.1130049 ±0.0000052	.1129779 ±0.0000050	.999615 ±0.000152	2.35 ±0.93
2,2,4,4-Tetramethylpentane.....	.1129624 ±0.0000102	.1129354 ±0.0000102	.999239 ±0.000171	4.65 ±1.04
2,3,3,4-Tetramethylpentane.....	.1130014 ±0.0000210	.1129734 ±0.0000214	.999575 ±0.000238	2.60 ±1.45

Compound	Heat of isomerization of the liquid, $H_i(\text{liq}) - H_n(\text{liq})$, at 25.00° C		Heat of combustion of the liquid, $-\Delta H_c^\circ$, at 25.00° C	
	<i>Int. kj/mole</i>	<i>kcal/mole</i>	<i>Int. kj/mole</i>	<i>kcal/mole</i>
<i>n</i> -Nonane.....	0.00	0.00	6123.51 ±0.75	1463.80 ±0.18
3,3-Diethylpentane.....	-0.02 ±1.39	-0.01 ±0.33	6123.49 ±1.58	1463.79 ±0.38
2,2,3,3-Tetramethylpentane.....	-2.92 ±1.31	-0.70 ±0.31	6120.59 ±1.51	1463.10 ±0.36
2,2,3,4-Tetramethylpentane.....	-2.35 ±0.93	-0.56 ±0.22	6121.16 ±1.19	1463.24 ±0.28
2,2,4,4-Tetramethylpentane.....	-4.65 ±1.04	-1.11 ±0.25	6118.86 ±1.28	1462.69 ±0.31
2,3,3,4-Tetramethylpentane.....	-2.60 ±1.45	-0.62 ±0.35	6120.91 ±1.63	1463.18 ±0.39

method of Washburn [13]; ² B_i/B_n° , which is equal to the ratio of the heat evolved, per mole of hydrocarbon, in the ideal bomb process at 28° C for each isomer to that of *n*-nonane; $(-\Delta U^\circ)_n - (-\Delta U^\circ)_i$, the difference, between *n*-nonane and each isomer, in the heat of combustion in the ideal bomb process at 28° C; $H_i^\circ(\text{liquid}) - H_n^\circ(\text{liquid})$, the heat of isomerization of *n*-nonane into each isomer, at 25° C and 1 atmosphere, for the liquid state; and $-\Delta H_c^\circ$, the decrement in the heat content accompanying the reaction of combustion of the hydrocarbon in the liquid state in oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard states at 25° C.

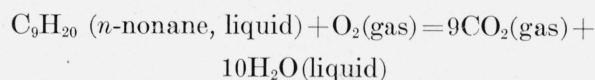
The value of the heat of isomerization was obtained by means of the relation [1]:

$$(-\Delta U^\circ)_n - (-\Delta U^\circ)_i = (-\Delta U^\circ)_n (1 - B_i^\circ/B_n^\circ).$$

For this calculation, the value of $(-\Delta U^\circ)_n$ at 28° C was taken as 6110.2 int. kj/mole [3]. The

² The Washburn correction is the same for all these compounds as they are isomers, but account is taken of the variation of the correction with the amount of sample burned. As used here, the Washburn correction was modified to apply to 28° C and to the gases at zero pressure (instead of 1 atmosphere).

value of the heat of combustion of a given isomer was obtained by appropriately combining the heat of isomerization with the heat of combustion of *n*-nonane as given by the equations [8]



$$\Delta H_{298.15}^\circ = -6123.51 \pm 0.75 \text{ int. kj/mole} = -1463.80 \pm 0.18 \text{ int. kcal/mole}.$$

All the uncertainties assigned to the experimental quantities in table 2 (except the heats of combustion) are equal to twice the standard deviation of the mean. The uncertainties assigned to the values of the heats of combustion were obtained by combining [11] the uncertainty in the value of the heat of combustion of *n*-nonane [8] with the uncertainties in the values of the heats of isomerization. The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may conservatively be taken as ±0.30 kcal/mole.

The experimental data of the present and previous investigations on the paraffin hydrocarbons are being correlated to yield heats of combustion

and formation of the remaining 29 nonanes which have not been subjected to experimental measurement, with general formulas for calculating values for the decanes and higher paraffin hydrocarbons [14].

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WASHINGTON, November 6, 1946.